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(54) Improvement in the copolymerisation of unsaturated esters.

(57) The reaction cycle time for the copolymerisation of unsaturated esters such as alkyl fumarates and vinyl acetate, and for the polymerisation of methacrylates and acrylates may be dramatically reduced by carrying out the polymerisation at elevated temperatures and pressures. An additional feature is the addition of initiator during polymerisation which leads to improved products especially for lubricating oil pour depressants and fuel and crude oil flow improvers.

Improvement in the Copolymerisation of Unsaturated Esters

- 1 The invention relates to a process for the preparation
of polymers and copolymers of unsaturated esters
especially for use as additives for liquid hydrocarbons
especially fuels and lubricating oils and the products
5 prepared thereby. Particularly the invention relates
to an improved process for the preparation of pour
point depressing additive materials for combination
with waxy mineral lubricating oils. More particularly
the invention relates to an improved process for the
10 preparation of pour point depressing lubricating oil
additive materials and additives for fuels and crude
oils by copolymerizing an ester of an unsaturated
polycarboxylic acid with a second polymerisable
material in the presence of a peroxide catalyst.
- 15 The art of additive manufacture for hydrocarbon fuels
and lubricants has long been familiar with the preparation
of polymers and copolymers to form materials useful for
improving desirable characteristics of the hydrocarbons
such as improving the viscosity index, that is, for
20 reducing the rate of change of viscosity of an oil with
a change in temperature and reducing the pour point of
hydrocarbon fuels including crude, residual and distil-
late oils. Such materials as polymers and copolymers of
acrylate esters, polymers and copolymers of alpha-beta

1 unsaturated poly-carboxylic acid esters, etc., have
been found to be very satisfactory for many purposes.
It has also been found, however, that the preparation
of these polymers and copolymers presents many
5 technical difficulties.

It has long been known to polymerise dialkyl fumarates
and vinyl acetate to produce copolymers suitable as
pour depressants for lubricating oils. Similarly it
has been known to copolymerise alkyl acrylates and
10 methacrylates of differing alkyl groups to produce
other copolymers useful as lubricant additives and
acrylates and methacrylates of varying compositions to
produce pour depressants for hydrocarbon fuels and
crude oils. To date these materials have been produced
15 by free-radical polymerisation at atmospheric pressure
and at a temperature around the normal boiling point of
the solvent. Whilst this technique has produced
satisfactory materials it suffers from the disadvantage
that the polymerisation time needed has been as high as
20 10 to 20 hours and that the products obtained can vary
by an undesirable amount. For example United States
Patent 2936300 shows copolymerisation of vinyl acetate
and alkyl fumarates using 5 to 15 hours.

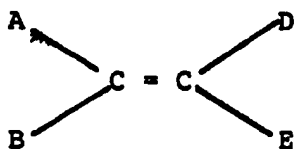
Typically the processes used have employed cyclohexane
25 as a solvent and have been carried out at atmospheric
pressure and around 85°C with a 15 hour cycle time.

- 1 We have now found that the polymerisation cycle time
may be dramatically reduced and the consistency of the
product improved if the polymerisation is carried out
under elevated pressure and at temperatures generally
5 above the normal boiling temperature of one or more of
the monomers. The pressure being sufficient to prevent
vapourisation of the monomers. This process also
allows reduced cycle times using volatile solvents
which are easily removed after polymerisation if the
10 pressure is high enough to prevent vaporisation of the
solvent during polymerisation. We have also found that
by using the higher pressures of the present invention
there is a greater flexibility to select the most
efficient initiator for the particular polymerisation.
- 15 In the previously proposed processes carried out at
atmospheric pressure all the initiator and the reactants
are injected into the reaction vessel at the start.
As a further feature the catalyst and some or all of
the reactants may be injected during the polymerisation
20 reaction which can give better control of the reaction.
- The present invention therefore provides a process for
the polymerisation or copolymerisation of unsaturated
esters comprising the free radical solvent polymerisation
under a blanket of an inert gas at a pressure in the

- 1 range 5 p.s.i. to 1600 p.s.i. and at a temperature in
the range 85° to 200°C preferably 90°C to 200°C and
using a free radical generating catalyst having a half
life no greater than 2 hours at the reaction temperature.
- 5 As a further feature of the present invention the free
radical generating catalyst is injected into the
reaction vessel during all or part of the reaction
time. If desired a monomer may also be injected
during the reaction.
- 10 The choice of the exact reaction conditions to be used
will depend upon the unsaturated esters being poly-
merised, the particular catalyst being used and the
properties desired in the product. We have found
however that in many instances the use of the process
15 of the present invention has the following significant
advantages over the previously used processes. The
reaction time may be reduced from 15 to 20 hours to, in
some instances, as little as one and a quarter hours.
We have also found that the new process allows improved
20 flexibility and better control of the specific
viscosity of the material obtained.

1 The present invention is applicable to many unsaturated
 ester but we are particularly concerned with the
 polymerisation and copolymerisation of acrylates and
 methacrylates and the copolymerisation of alkyl fumarates
 5 and vinyl acetate to produce those materials which find
 widespread use as pour depressants in lubricating
 oils and hydrocarbon fuels.

Unsaturated di- and tri-carboxylic acid esters which
 may be polymerised according to the present invention
 10 include those represented by the following formula



wherein

15 (1) A and D are carboxylic acid ester groups



and B and E are hydrogen, e.g., fumaric acid esters,
 maleic acid esters, etc., or

20 (2) A and D are carboxylic acid ester groups, as
 above, and either B or E is a methyl group, the other
 being hydrogen, e.g., citraconic acid esters, mesaconic
 acid esters, etc., or

(3) A and B are hydrogen, D is a carboxylic acid ester
 25 group and E is a methylene carboxylic acid ester group,
 e.g., itaconic acid esters, or

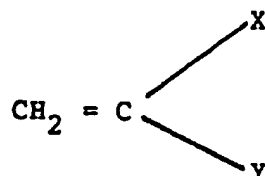
- 1 (4) A and D are carboxylic acid ester groups as above,
E is a methylene carboxylic acid ester group and B is
hydrogen, e.g., aconitic acid esters.

5 It will be noted that the unsaturation in all of these
compounds is alpha-beta to at least one carboxy group.
Although any of the carboxylic acid esters, according
to the formula above, or mixtures of such polycarboxylic
acid esters, are operable in the process of this
invention, the fumaric acid esters and maleic acid
10 esters are particularly advantageous. Mixtures of two
or more of such unsaturated polycarboxylic acid esters
in varying proportions, i.e., 10-90 parts fumaric and
90-10 parts maleic ester, may be used in place of only
one ester.

15 The esters may be prepared by esterification of any of
the unsaturated polycarboxylic acids or their anhydrides
with alcohols selected from the C₁ to C₃₀ aliphatic
alcohols and mixtures thereof. Primary alcohols are
preferred over secondary and tertiary alcohols, although
20 secondary alcohols are sometimes suitable. The alcohols
are preferably saturated, although some degree of
unsaturation is permissible when mixtures of alcohols
are employed. Straight chain or lightly branched
alcohols are preferred over highly branched alcohols.

1 These unsaturated carboxylic acid ester may readily be
copolymerised by the process of the present invention
with other polymerizable monomeric materials. These
monomers may be represented by the following formula:

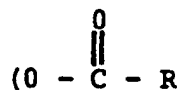
5



wherein

(1) X is hydrogen and Y is an ester group

10



R being methyl, ethyl, butyl and the like) e.g., vinyl
acetate, vinyl butyrate and the like, or

(2) X is methyl, ethyl, etc., and Y is as described
15 above, e.g. isopropenyl acetate, etc., or

(3) X is halogen and Y is as described above, e.g.
alpha-chlorovinyl acetate, etc., or

(4) X is a hydrogen or methyl and Y is an aromatic
group, e.g., styrene, alpha-methyl styrene, and the
20 like, or

(5) X is hydrogen or methyl and Y is $-\text{C} = \text{N}$, e.g.,
acrylonitrile, etc.

1 Although any of the polymerizable monomeric materials
typified by the formula above are operable to form
useful copolymers with carboxylic acid esters
outlined above, the preferred embodiment contemplates
5 the use of vinyl compounds, particularly vinyl esters
and their substitution products. Vinyl fatty acid
esters containing from about 2 to about 18 carbons are
particularly operable, such as vinyl acetate, vinyl
propionate, vinyl butyrate, vinyl laurate, vinyl
10 stearate and the like. Mixtures of such vinyl esters,
e.g., 10-90 parts of vinyl acetate and 90-10 parts of
isopropenyl acetate, may be used in place of a rela-
tively pure vinyl ester. Vinyl acetate is particularly
preferred.

15 The invention is equally applicable to the copolymeri-
sation of alkyl fumarates and vinyl acetate to produce
materials useful as pour depressants in lubricating
oils or flow improvers for fuels and crude oils.
Also the polymerisation or copolymerisation of alkyl
20 acrylates and methacrylates to produce heavy fuel and
crude oil flow improvers, viscosity index improvers and
pour depressants for lubricating oils, the copolymers
of alkyl methacrylates being particularly useful as
viscosity index improvers for automatic transmission
25 fluids. The monomers to be polymerised will be
selected according to the desired use of the polymer.

1 The products of the present invention are particularly
useful as lubricant additives where they find use as
viscosity index improvers and pour point depressants
and as flow improvers for fuels. We also find that the
5 improved control allowed by the process of the present
invention allows products of better consistency and
hence improved potency as lubricant additives to be
obtained. The products may be used in conjunction with
other conventional lubricant additives such as disper-
10 sants, viscosity index improvers, viscosity index
improver dispersants, antiwear additives such as the
zinc dialkyl dithiophosphates and metal containing
detergents such as the basic alkaline earth metal
sulphonates and phenates.

15 The present invention is illustrated by reference to
the following Examples in which the fumarate ester used
in Examples 1 to 7 was a mixed C₈ to C₁₈ linear
dialkyl fumarate and the initiator was tertiary butyl
peroctoate. The polymerisations were carried out under
20 a blanket of nitrogen and in Examples 1 to 4 they were
carried out in a 3 litre reactor and in Examples 5 to 7
in a ten cubic metre reactor. The conditions, quantities
of material used and materials obtained in Examples 1
to 4 are given in Table 1 and those for Examples 5 to 7
25 in Table 2. Soak being the time allowed after completion
of catalyst and monomer injection before the reaction
was terminated.

The process used was as follows:

<u>Example</u>	1	2	3	4
<u>Polymerisation Conditions</u>				
Temperature, °C	110	110	110	110
N ₂ pressure, psig	90	90	90	90
Time, mins: Injection	120	120	120	120
Soak	15	15	15	15
<u>Charged to Reactor</u>				
fumarate ester (grms)	1311	1311	1311	1311
vinyl acetate (grms)	67.7	67.7	67.7	67.7
cyclohexane (grms)	208	208	312	312
<u>Injected during reaction</u>				
vinyl acetate (grms)	244.5	244.5	244.5	244.5
t-butyl peroactate "	4.0	4.0	4.0	4.0
in cyclohexane (grms)	43.2	43.2	43.2	43.2
<u>Results</u>				
Yield(1) grms polymer	1469	1476	1493	1480
grams of active ingredient per 100 grams of fumarate ester charged	102.3	102.2	102.3	100.6
Dialysis: wt% residue	91.3	90.8	90.7	89.1
Free fumarate in polymer, wt.%	<0.1	<0.1	<0.1	<0.1
Fumarate conversion, %	>99.9	>99.9	>99.9	>99.9
Specific Viscosity (2) of stripped polymer:				
wt/vol	0.26	0.29	0.24	0.21
of dialysed residue:				
wt/vol	0.30)	0.33)	0.26)	
	0.31)	0.32)	0.26)	0.23
wt/wt	0.25	0.24	0.20	0.20

Table 2

<u>Example</u>	5	6	7
<u>Polymerisation Conditions</u>			
Temperature, °C	110	110	110
N ₂ pressure, psig	90	90	90
Time, mins: Injection	120	120	120
Soak	15	15	15
<u>Charged to Reactor</u>			
fumarate ester(Kilograms)	3700	3700	4810
vinyl acetate (Kilograms)	191	191	247
cyclohexane (Kilograms)	587	587	1145
<u>Injected during reaction</u>			
vinyl acetate (Kilograms)	690	690	897
t-butyl peroactate "	11.4	11.4	14.8
in cyclohexane(Kilograms)	124	124	161
<u>Results</u>			
Yield Kilograms polymer	-	-	1476
grams of active	105	over all	105 over all
ingredient per 100 grams	3	batches	3 batches
of fumarate			
ester changed			
Dialysis: wt% residue	97.4	95.0	89.6
Free fumarate in			
polymer, wt.%	<0.1		
Fumarate conversion,%	>99.9		
Specific Viscosity (2)			
of stripped polymer:			
wt/vol	0.35	0.34	0.23
of dialysed residue:			
wt/vol	0.32		0.20
wt/wt	0.31	0.31	0.22

- 1 The effectiveness of the products of Examples 5 and 6
as pour point depressants were tested in five typical
European multigrade lubricating oils, in a bright stock
lubricating oil and in two typical European multigrade
5 oils and the average pour depression obtained was found
to be as follows:

	wt%	Pour Depression	
		Example 5	Example 6
10	Additive		
	0.2	13.3	13.5
	0.3	16.7	16.0
	0.4	17.5	19.2

1 Examples 8 to 13

A series of polymethacrylates were prepared in the 3 litre reactor used in Example 1 with a 75 minute reaction time and continuous injection of the initiator for 1 hour followed by a soak time. The solvent was cyclohexane and the initiator t-butylperoctoate and polymerisation temperatures of 120° and 135°C were used under a nitrogen pressure of 90 psi.

The results of the polymerisation reactions are shown in Table 2.

The alkyl ester of the methacrylate was straight chain and their composition was:

	<u>Alkyl Group</u>	<u>wt. %</u>
	C ₁₀	2.5
15	C ₁₂	55.5
	C ₁₄	21.3
	C ₁₆	10.7
	C ₁₈	10.0

Table 2Polymer Preparation and Properties

Example	Temp., °C	Soak time, mins	Mole ratio monomer/ cyclohexane	Mole ratio initiator/ monomer $\times 10^3$	Polymer sp. vis. (2 wt/vol% in toluene at 40°C)
8	135	10	0.06	7.4	0.14
9	135	10	0.24	7.4	0.33
10	135	10	0.47	7.4	0.61
11	135	10	0.93	7.4	1.54
12	120	15	0.47	7.4	0.74
13	120	15	0.93	7.4	1.84

The solvent and monomer were charged to the autoclave and the initiator was injected at a steady rate during the injection time.

1 Examples 14 to 18

 A series of polymethacrylates were prepared in the 3
litre reactor used in Example 1 with a 75 minute
reaction time and continuous injection of the
5 initiator for 1 hour followed by a soak time. The
solvent was cyclohexane and the initiator
t-butylperoxide, the polymerisation temperature
120°C under a nitrogen pressure of 90 psi.

 The results of the polymerisation reactions are
10 shown in Table 3.

Table 3

Example	Monomer	Mole ratio monomer/ cyclohexane	Mole ratio initiator/ monomer $\times 10^3$	Polymer sp. vis. (2 wt/vol% in toluene at 40°C)
14	dodecyl acrylate	0.47	7.4	0.25
15	dodecyl acrylate	0.91	7.4	0.37
16	stearyl acrylate	0.91	7.4	0.49
17	stearyl acrylate	0.91	0.93	0.59
18	stearyl acrylate	1.72	0.93	0.94

CLAIMS

- 1 1. A process for the polymerisation or copolymerisation of unsaturated esters comprising free radical solvent polymerisation under a blanket of an inert gas at a pressure in the range 5 p.s.i.
5 to 1600 p.s.i. and at a temperature in the range 85°C to 200°C and using a free radical generating catalyst having a half life no greater than 2 hours at the reaction temperature.
2. A process according to claim 1 in which the
10 temperature is in the range 90°C to 200°C.
3. A process according to claim 1 or claim 2 in which the free radical generating catalyst is injected into the reaction vessel during all or part of the reaction time.
- 15 4. A process according to any of the preceding claims in which monomer is injected into the reaction vessel during the reaction.
5. A process according to any of the preceding
20 claims where the esters are acrylates or methacrylates.

- 1 6. A process according to any of the claims 1 to
 4 in which vinyl acetate and alkyl fumarates are
 copolymerised.
7. Polymers and copolymers of unsaturated esters
5 wherever produced by a process according to any
 of the preceding claims.
8. The use as additives for liquid hydrocarbons of
 the polymers and copolymers of claim 7.